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Synthesis of novel nanoreinforcements for polymer matrices by ATRP: Triblock poly(rotaxan)s based in polyethyleneglycol end-caped with poly(methyl methacrylate)

Verónica San-Miguel, María González, Javier Pozuelo*, Juan Baselga

Departamento de Ciencia e Ingeniería de Materiales e Ingeniería Química, Universidad Carlos III de Madrid (IAAB), Av. Universidad 30, 28911 Madrid, Spain

Poly(rotaxan)s of poly(ethylene glycol) and α cyclodextrines (CD) block copolymers end capped with poly(methyl methacrylate) chains were synthesized by atom transfer radical polymerization. The synthesized copolymers were characterized by ^{1}H NMR, 2D NOESY NMR, X ray and Thermogravimetric analysis. Assuming a maximum relation of 2 CDs per ethyleneglycol unit, a coverage degree of 18% and 15% was achieved. X ray analysis showed a characteristic signal around 20θ for all copolymers with an amorphous halo mainly due to inter crystal poly(ethylene glycol) and poly(methyl methacrylate) chains. Full Molecular Dynamics of 20 ns was used to simulate the crystal structure of these copolymers. A pair correlation function was used to determine the coupling between hydrogen atoms of PEG, PMMA and cyclodextrine obtained by 2D NOESY NMR.

Keywords: Poly(rotaxan)s; Nanoreinforcement; Atom transfer radical polymerization

1. Introduction

It is generally accepted that effects caused by nanoreinforcement on polymer matrices are produced with very small amounts as compared with traditional polymeric composites. Their small size has two main consequences: (i) interfacial surface to volume ratio is very high, magnifying the influence of the surface properties of reinforcements (ii) the distance between particles is very small (around the relaxation volume of polymer chains), so almost the whole volume of the polymer matrix is under the influence of the reinforcement. These two aspects enhance the trend to nanoparticle self aggregation, making sometimes necessary a surface treatment during their preparation to get good dispersions into polymeric matrices.

A large number of materials has been produced by introducing nano objects of various shapes into polymer matrices. In this way, whiskers (carbon or glass fibres, rigid rod like molecules, carbon nanotubes, cellulose whiskers, etc) or platelets (talcum powder or bentonite minerals, clay or mica flakes, etc.) have been explored [1 10]. One of the key factors in the preparation of polymer nanocomposites is the aspect ratio of the nanoreinforcement. It has been determined that maximum values of Young Modulus are obtained for aspect ratios around 200 [11]. The synthesis of high aspect ratio nanoparticles that will be introduced in a polymer matrix is one of the most cumbersome steps in the preparation of new materials due to the need of surface modifications to produce interfaces not impacting negatively the matrix properties to be improved.

Cyclodextrines (CDs) are cyclic oligosaccharides formed by six or more D+ glucopyranose units connected by α 1,4 linkages. The best known are those formed by six to nine glucose units called α (6), β (7), γ (8) and δ (9) CD respectively. It is generally accepted that Van der Waals interactions play an important role in host guest associations between cyclodextrines and small molecules [12,13] or polymers [14,15] where the hydrophobic properties of the inner cavity of cyclodextrines are of great importance [16,17].

Around the 90's, Harada et al. prepared poly(rotaxan)s between a wide number of polymers and cyclodextrines [18 25] such as complexes of α cyclodextrine with poly(ethylene glycol) [18,20,22]. ^{13}C CP/MAS NMR and X ray spectra of these complexes suggest that cyclodextrines are threaded along the polymer chain creating a "channel type" structure which was described by Mc Mullan et al. [26]. Other authors (Wenz [27,28], Topchieva and Tonelli [29,30]) have also studied this kind of complexes as well as poly(rotaxan)s formed by direct complexation of CD's with block copolymers [31,32]. We have studied the stoichiometry and rigidity of some of these compounds by Molecular Dynamics [14,15]; their high aspect ratio, their low conformational flexibility along with plenty of functional groups over which a rich chemistry can be done to couple them to polymer matrices make them good candidates as

* Corresponding author. Tel.: +34 91 6249940; fax: +34 91 6249430.
E-mail address: jpozue@ing.uc3m.es (J. Pozuelo).

nanoreinforcements. Nevertheless, the biggest handicap of this kind of complexes for this application is twofold. On the one hand, the high number of hydroxyl groups on their surface facilitates self aggregation forming molecular crystals; this fact adds an extra interaction energy between complex molecules preventing its dispersion in polymer matrices. On the second hand, and also due to the high concentration of hydroxyl groups, the fact that these complexes only dissolve in highly polar solvents (DMSO, DMF,…) [20,22] points to the unfavourable interactions between the complexes and polymers, which also hinders preparation of good dispersions.

In the present work, we have synthesized and characterized poly(rotaxan)s of poly(ethyleneglycol) with α CD with high aspect ratios. Molecular dynamic simulations have also been performed to shed light on to some aspects of the behaviour of this kind of compounds. It is well known this kind of complexes show a high tendency to uncomplexation when the solvent is not water; traditionally "end capping" has been used as a strategy to avoid this phenomenon [20]. Some authors have end capped the pseudo poly(rotaxan)s extending the chains by copolymerizing water soluble monomers via ATRP. In this way, poly(rotaxan)s as central blocks having blocks of poly(2 hydroxyethyl methacrylate) [33,34], (2 hydroxypropyl methacrylate) [35], poly(2 (dimethylamino)ethyl methacrylate) [36] and poly(ethylene glycol) methyl ether methacrylate [37] has been reported.

In this work, PMMA chains have been polymerized at the ends of the poly(rotaxan)s by Atom Transfer Radical Polymerization, yielding "triblock copolymers". It is well known that PMMA is highly miscible with some thermoplastics, such as poly(vinylidene fluoride) [38], copolymers like SAN (Styrene acrylonitrile) [39] and SMA (Styrene maleic anhydride) [40], and also with the commonly used DGEBA epoxy resin [41] with which no phase separation has been observed during curing with certain hardeners. Thus, PMMA blocks can be expected to play two important roles: (i) to improve the miscibility of poly(rotaxan)s with polymeric matrices and (ii) to stabilize the inclusion complexes acting as end cappers. Wang et al. reported the use of PEG αCD poly(rotaxan)s to improve mechanical properties of brittle Novolac epoxy resins [42], although phase separation was observed at high poly(rotaxan)s compositions. Park et al. incorporated PEG (PPG αCD) PEG in a polyurethane matrix and reported an increased toughness of the final material [43]. The high miscibility of PMMA blocks with a wide variety of polymer matrices combined with the high aspect ratio of the PEG inclusion complexes makes PMMA PEG PMMA based poly(rotaxan)s good candidates for effective polymer reinforcement, since PMMA blocks provide improved matrix reinforcement interactions and facilitates the dispersion of the poly(rotaxan)s.

2. Experimental details

2.1. Materials

Poly(ethylene glycol) (PEG) (Fluka, M_n 3000 g/mol and M_n 6000 g/mol), 2 bromoisobutyryl bromide (Aldrich, 98%), triethyl amine (TEA) (Aldrich, 99%), *N*,*N*,*N*′,*N*′,*N*″ pentamethyldiethylentriamine (PMDTA) (Aldrich, 99%) and tetrahydrofuran (THF) (anhydrous, Aldrich, >99.9%) were used as received without further purification. The α cyclodextrine (α CD) purchased from Wacker was dried under vacuum overnight at 80 °C prior to use. Methyl methacrylate (MMA, Aldrich, 99%) was purified by passage through a short column of activated basic alumina before using to remove inhibitors and acidic impurities. Copper bromide (Cu(I)Br) (Aldrich, 99%) was purified according to the method of Keller and Wycoff [16]. *N*,*N* Dimethylformamide (DMF) (Scharlau, 98%) was degassed by bubbling nitrogen for thirty minutes and in all experiments MilliQ grade water was used.

2.2. Synthesis of poly(ethylene glycol) methyl ether 2 bromoisobutyrate

2 Bromoisotutyryl bromide (0.72 mL, 3.0 mmol) and triethyl amine (0.84 mL, 3.0 mmol) were added dropwise to an anhydrous THF solution (150 mL) of poly(ethylene glycol) (PEG) (M_n 3000 g/mol) (6.0 g) under nitrogen atmosphere at 0 °C. The reaction was carried out at ambient temperature overnight. The precipitated salts were removed via filtration and volatiles eliminated under reduced pressure. The obtained viscous oil product was dissolved in dichloromethane and washed with a saturated $NaHCO_3$ solution. The organic phase was dried over anhydrous magnesium sulphate and filtered. The white solid was eluted through a basic alumina column with dichloromethane and the solvent was removed under vacuum (yield 84%).

2.3. Preparation of pseudo poly(rotaxan)s based on poly (ethylene glycol)

Inclusion complex of α CDs with PEG_{3000} was obtained by adding an aqueous solution of poly(ethylene glycol) methyl ether 2 bromoisobutyrate (1 g, 0.31 mmol) to a saturated solution of α CD (6 g, 6.12 mmol) in 57 mL of water at room temperature. The mixture was vigorously stirred during 48 h. Then, it was centrifuged and washed with water three times to eliminate the free α CDs. Finally, the suspension was lyophilized in order to obtain a quantitative white solid.

2.4. Synthesis of triblock poly(rotaxan)s by ATRP

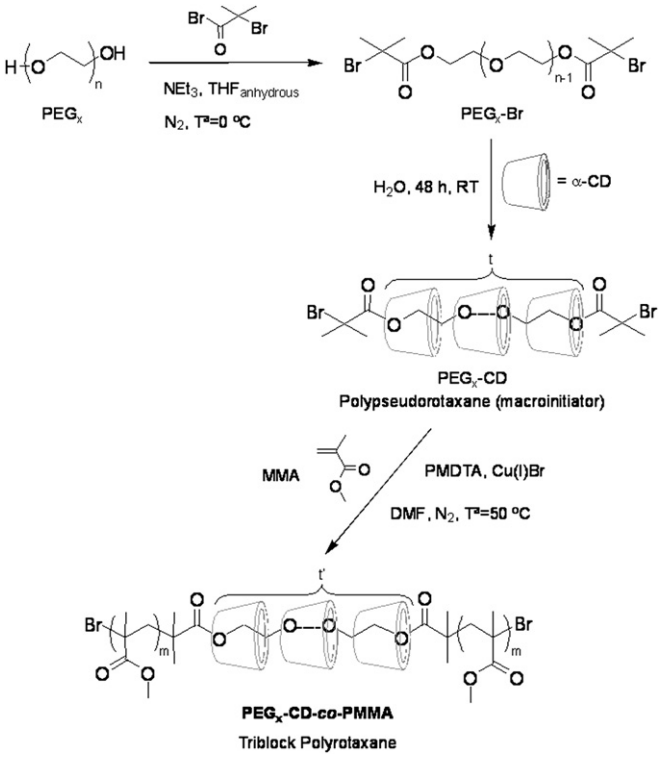
Two triblock poly(rotaxan)s were synthesized by copper mediated living radical polymerization using pseudo poly(rotaxan)s as macroinitiators and methyl methacrylate. Pseudo poly(rotaxan)s based on poly(ethylene glycol) were obtained from PEG with a molecular weights of 3000 g/mol (PEG_{3000} CD) and 6000 g/mol (PEG_{6000} CD) and they constitute the central block of the triblock. The complete synthesis of poly(rotaxan)s was accomplished following the route shown in Scheme 1.

Methyl methacrylate (0.47 mL, 4.40 mmol) was placed in a Schlenk tube and dissolved in deoxygenated *N*,*N*′ dimethylformamide (7 mL). PMDTA (92 μL, 0.440 mmol) was added to the solution. Then, the tube was sealed with a rubber septum and the mixture degassed *via* three freeze pump thaw cycles. PEG_{3000} CD macroinitiator (1.0 g, 0.044 mmol) and Cu(I)Br (13 mg, 0.088 mmol) were added to the frozen mixture and the system was deoxygenated by three vacuum N_2 cycles. The reaction mixture, under nitrogen, was placed in an oil bath at 50 °C.

After 6 h, polymerization was finished by dilution with DMF and exposing the mixture to air, leading to aerial oxidation of the catalyst. The solvent was removed under reduced pressure. The solid was centrifuged several times with Milli Q water in order to eliminate catalyst residues and free a CDs which could have unthreaded during the polymerization process. The resulting white product was obtained by lyophilisation. Triblock poly(rotaxan)s were named as PEG_x CD *co* PMMA, where *x* stands for the PEG molecular weight.

2.5. Characterization methods

^{1}H NMR and 2D NOESY NMR were recorded on a Bruker AM 500 instrument at room temperature using DMSO d_6 as solvent. Wide angle X ray diffraction (WAXRD) measurements were



Scheme 1. Synthetic route of triblock poly(rotaxan)s based on poly(ethylene glycol). In the scheme *t* and *t'* indicate the number of α-CDs threaded onto a PEG chain in the pseudo-poly(rotaxan)s and triblock poly(rotaxan)s, respectively.

performed on powder samples using Panalytical X'pert Pro X ray diffractometer. The radiation source used was Ni filtered, Cu Kα radiation with a wavelength of 0.154 nm, the voltage was set to 40 KV and the current to 40 mA. Samples were placed on a sample holder and scanned from 5° to 40° in 2θ at a scan speed of 0.020 °/s. Thermogravimetry (TGA) measurements were per formed in a PerkinElmer TGA7 model thermobalance. Measure ments were carried out using 5 mg samples and heated at a rate of 10 °C/min under nitrogen atmosphere. Thermal transitions were determined by Differential Scanning Calorimetry (DSC). A Mettler Toledo 822 calorimeter equipped with a liquid nitrogen reservoir was used. Samples were placed in sealed Al pans and two scans from 70 °C to 200 °C at 10 °C/min were performed on each sample. In order to minimize the effects of previous thermal history, data from the second scan were used for analysis.

3. Computational details

Structures of PEG_{3000} CD *co* PMMA and PEG_{6000} CD *co* PMMA copolymers were generated and simulated with Accelrys commercial software (Materials Studio 3.2) with PEG in *all trans* conformation with α CD *head to tail* orientation uniformly distributed around the PEG chain [44] using the COMPASS force field [45]. All the MD simulations were performed under NVT conditions at 500 K controlled by means of the Andersen thermo static method with a collision ratio of 1.0. A time step τ 1 fs (i.e. 10 15 s) for the integration of the atomic motion equations was used. The Van der Waals and coulombic non bonding interactions were calculated by the cell multipole method (CMM) [46 48]; the value of the updated width parameter was 1.0 Å, and the accuracy parameter was set to medium to use 3rd order in the Taylor series expansion and explicit interactions from more neighbouring cells. The structure of each system was first minimized with respect to all the internal coordinates by a Conjugate Gradient method until the maximum derivative was smaller than 0.1 Kcal/(Å mol), with a limit of 5000 steps. The system was submitted to an equilibration process consisting on a 15 ns (1.5×10^{-8} s) long MD run. The data collecting stage consisted on a 5 ns (5×10^{-9} s) MD run for the two systems. In both cases, the trajectories were saved every 500 fs for subsequent analysis.

Molecular weights of the poly(rotaxan)s copolymers were calculated by molecular dynamic simulations. Fig. 1 shows the energy history for 20 ns trajectories of all poly(rotaxan)s. The crystalline structures of PEG_{3000} CD *co* PMMA and PEG_{6000} CD *co* PMMA were obtained after 5 ns and 15 ns respectively, and they were used for subsequent analysis.

The distribution of hydrogen atoms in the conformational landscape of the copolymers was investigated by computing intermolecular pair correlation functions $g_{AB}(r)$, which represent the probability of finding a pair of *AB* atoms at a distance $r \pm dr$. Values of $g_{AB}(r)$ were evaluated as [44]:

$$g_{AB}(r) \quad \frac{\left\langle \sum_{i \neq j} \delta(r \quad |r_{Ai} \quad r_{Bi}|) \right\rangle}{\sum_{r} g_{AB}(r)} \tag{1}$$

where *A* and *B* represent two types of particles (i.e. individual atoms). Vectors r_{Ai} and r_{Bj} represent the positions of *A* type particle "*i*" of and *B* type particle "*j*", so that $|r_{Ai} \quad r_{Bj}|$ is the distance between those two particles. The term $\delta(r \quad |r_{Ai} \quad r_{Bj}|)$ in equation (1) is set to one when $(r \quad |r_{Ai} \quad r_{Bj}|) \leq dr$ (i.e. when the difference

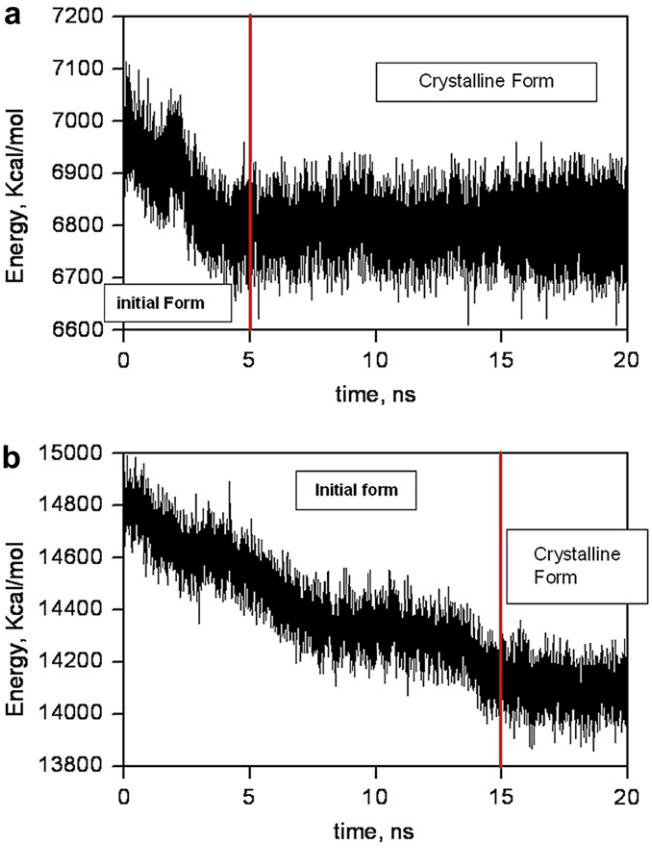


Fig. 1. Energy history of molecular dynamics simulations, (a) PEG_{3000}-CD-*co*-PMMA, (b) PEG_{6000}-CD-*co*-PMMA.

between the desired and actual distance among the two particles is smaller than a tolerance factor *dr*) and to zero otherwise.

4. Results and discussion

4.1. Synthesis of poly(rotaxan)s

Formation of pseudo poly(rotaxan)s with cyclodextrines proceeded by threading of a polymer backbone in aqueous solution, followed by aggregation of the threaded segments and precipita tion of a solid inclusion complex. Some important factors in the living radical polymerization with poly(rotaxan)s as macroinitiator: (i) The solvent can originate a substantial unthreading of α CDs from polymer molecular backbones. (ii) The monomer used as end cap can form molecular complexes with α CDs and not participate in the end capped polymerization. (iii) The ligand used in the PMMA polymerization can form complexes with α CDs and has to be fast enough to avoid unthreading during the living radical polymerization.

DMSO is a good solvent of pseudo poly(rotaxan) inclusion complexes of PEG and α CDs, but dissolution of these complexes in this solvent could result in a substantial unthreading of α CDs from PEG molecular backbone. Therefore polymerization reaction was carried out in DMF, since the macroinitiator is soluble in this solvent and α CDs will unthread slower than in DMSO. Pseudo poly(rotaxan)s prepared from PEG and α CDs were used as macroinitiators in the living radical polymerization. Polymerization of methyl methacrylate at the extremes of pseudo poly(rotaxan)s macroinitiators is expected to lead to end capped poly(rotaxan)s. For this purpose, a molar ratio $[MMA]_0/[\text{pseudo poly(rotaxan)}]_0$ 100/1 was selected to ensure long PMMA blocks.

It was assumed that free α CDs could be present in the reaction medium, so atom transfer radical polymerization should be carried out as fast as possible. *N,N,N′,N′,N″* pentamethyldiethylentriamine (PMDTA) was described earlier in the literature as a very reactive ligand [49,50] and its size and structure could prevent its introduction in free α CDs inner cavity. Therefore, a high concen tration of PMDTA was added to the reaction medium (relation ratio of Cu(I)Br:PMDTA 1:5), leading besides to an increase of poly merization rate [51].

The number of α cyclodextrines threaded onto a PEG chain in the macroinitiators (*t*) and in the poly(rotaxan)s (*t′*) are shown in Table 1, along with the polymerization degree of methyl methac rylate in the triblock copolymer, molecular weight of pseudo pol y(rotaxan)s and copolymers, percent α CD coverage and yield. The average number of α CD threaded into a PEG chain was estimated by comparing the integral values of C1 H of α CD at 4.76 ppm and O CH_2 CH_2 of PEG at 3.47 ppm. The coverage of α CD was calculated from the stoichiometry, in which two ethylene glycol units of PEG were assumed to be equal to the depth of the α CD inner cavity (ca. 7.9 Å). The yields in Table 1 represent the final masses of PEG_x CD and PEG_x CD *co* PMMA produced from the respective PEG and pseudo poly(rotaxan).

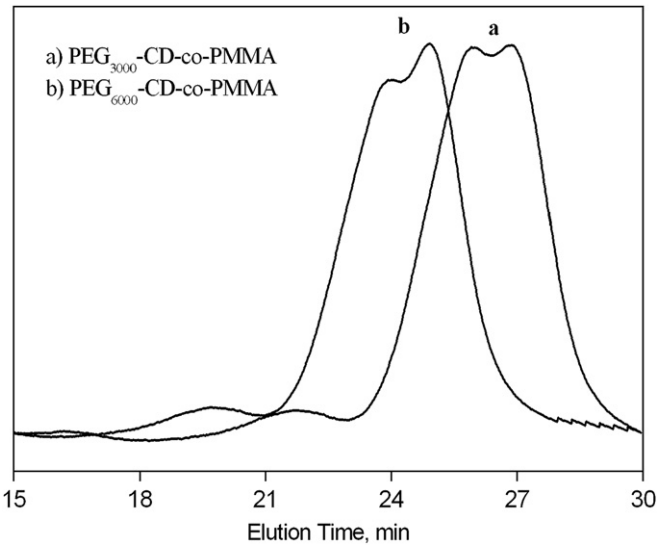


Fig. 2. GPC traces of PEG_{3000}-CD-*co*-PMMA and PEG_{6000}-CD-*co*-PMMA in DMF.

It can be observed that the number of α CDs threaded onto the bigger PEG backbone (PEG_{6000}) was higher than on the shorter PEG chain (PEG_{3000}). This result could lead to an improvement of mechanical properties compared to those of PEG_{3000} CD *co* PMMA copolymer.

Nevertheless, size exclusion chromatography (SEC) of poly (rotaxan)s performed in DMF reveals a bimodal pattern, as can be seen in Fig. 2. Both samples present almost the same polydispersity index: 1.69 and 1.73 for PEG_{3000} CD *co* PMMA and PEG_{6000} CD *co* PMMA, respectively. Molecular weights extracted from PS stan dards were lower than obtained from ^{1}H NMR probably due to the amphiphilic character of the synthesized poly(rotaxan)s, that could present globular states in DMF solvent.

In the ATRP initiation, the system has one competitive reaction that is the unthreading of some cyclodextrines from the PEG central block. This originates steric impediments slowing down or even blocking the initiation reaction. To avoid unthreading, an excess of the PMDTA was used, which has the effect of accelerating the polymerization. The lowered initiator efficiency joined with a faster propagation may justify the appearance of bimodal distributions [52] [G Moad, DH Solomon, "The chemistry of Radical Polymeri zation", Elsevier, Oxford, UK (2006 p 490).

4.2. NMR characterization

In general, the ^{1}H NMR spectra of the pseudo poly(rotaxan)s in DMSO seem to be identical to those of a physical blend of their two

Table 1
Pseudo-poly(rotaxan)s from PEG and triblock poly(rotaxan)s synthesized by atom transfer radical polymerization.

Name	α-CD/PEG[a] (mol/mol)	DP_{MMA}[b]	M_n[c] (g/mol)	Coverage[d] (%)	Yield[e] (%)
PEG_{3000}-CD	18	–	20,700	55	99
PEG_{6000}-CD	24	–	29,600	35	85
PEG_{3000}-CD-*co*-PMMA	6	28	12,000	18	36
PEG_{6000}-CD-*co*-PMMA	10	78	24,000	15	40

[a] The average number of α-CDs per PEG chain obtained from ^{1}H NMR.
[b] Total degree of polymerization of MMA in the triblock copolymer determined by ^{1}H NMR.
[c] Molecular weights calculated by ^{1}H NMR from the following equations: $M_n(\text{pseudo} - \text{poly(rotaxan)})$ $M_{n,PEG_x} + (M_{w,\alpha\ CD} \times n^{\circ}\alpha - CD_{threaded})$ $M_n(\text{poly(rotaxan)})$ $[([\text{Monomer}]_0 \times M_{w,monomer} \times \text{conversion})/[\text{Macroinitiator}]_0] + M_{n,PEG_x} + (M_{w,\alpha\ CD} \times n^{\circ}\alpha - CD_{threaded})$
[d] Coverage $2[(\alpha - \text{CD perchain})/(\text{PEG repeatunits})]$.
[e] Yield based on final product to total feed masses.

components, indicating that they actually exist as a dynamical mixture of threaded and unthreaded species. In contrast, previous studies demonstrated that formation of poly(rotaxan)s leads to broadened peaks, attributed to the decrease in conformational flexibility caused by blocking the dethreading of α CDs from PEG axle [49]Fig. Spectra of synthesized poly(rotaxan)s showed broader peaks in a 3.0 4.0 ppm range compared to that of pseudo poly (rotaxan)s (Fig. 3). Moreover, the peaks attributed to PMMA blocks were definitely observed in these triblock copolymers (δ 0.71 1.10 (m, 3 H × 28, CH_3); δ 1.77 1.86 (m, 2 H × 28, CH_2) and δ 3.55 (m, 3 H × 28, OCH_3)).

The interaction between α CD and PEG in the poly(rotaxan)s was evaluated using NOE analysis which provides information about the proximity of pairs of the PEG protons to the CD protons. Fig. 4 shows the 2D NOESY NMR spectra of the poly(rotaxan)s. The spectra show that the signals of C**3** H and C**5** H protons of α CD, which are directed towards the cavity, correlate with the resonance of the CH_2 of PEG; but the C**1** H, C**2** H and C**4** H protons, which are located outside the cavity, do not correlate with PEG. These results indicate that a PEG chain is included in α CD cavities.

The distribution of hydrogen atoms in the conformational landscape of the copolymers was investigated by computing intermolecular pair correlation function $g_{AB}(r)$ which represent the probability of finding a pair of *AB* atoms at a distance $r \pm dr$. Coupling signals obtained by 2D NOESY NMR are related with relative hydrogen distances lower than 2.5 Å. Therefore, the integral of the distribution, g_{AB}(r), for values smaller than 2.5 Å, should be proportional to the 2D NOESY NMR signals in the spectra.

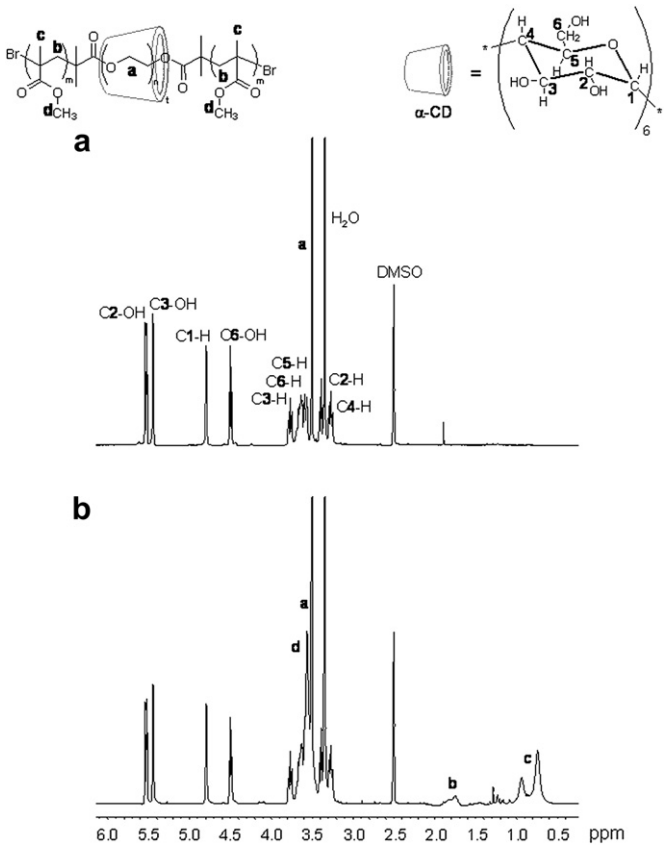


Fig. 3. ^{1}H NMR spectra of (a) pseudopoly(rotaxan) prepared by threading α-cyclodextrine onto PEG_{6000} and (b) poly(rotaxan) PEG_{6000}-CD-*co*-PMMA. **^{1}H NMR** (500 MHz, DMSO-d_6), δ (ppm): 0.71–1.10 (m, 3 H × 28, CH_3 of PMMA), 1.77–1.86 (m, 2 H × 28, –CH_2– of PMMA), 3.33 (m, 6 H × 6, C4-H of α-CD), 3.41 (m, 6 H × 6, C2-H of α-CD), 3.51 (m, 4 H × 68, –CH_2CH_2O– of PEG), 3.55 (m, 3 H × 28, –OCH_3– of PMMA), 3.55 (m, 18 H × 6, C5-H, C6-H of α-CD), 3.77 (m, 6 H × 6, C3-H, of α-CD), 4.48 (t, 6 H × 6, C6-OH of α-CD), 4.80 (d, 6 H × 6, C1-H of α-CD), 5.44 (d, 6 H × 6, C3-OH of α-CD), 5.50 (d, 6 H × 6, C2-OH of α-CD).

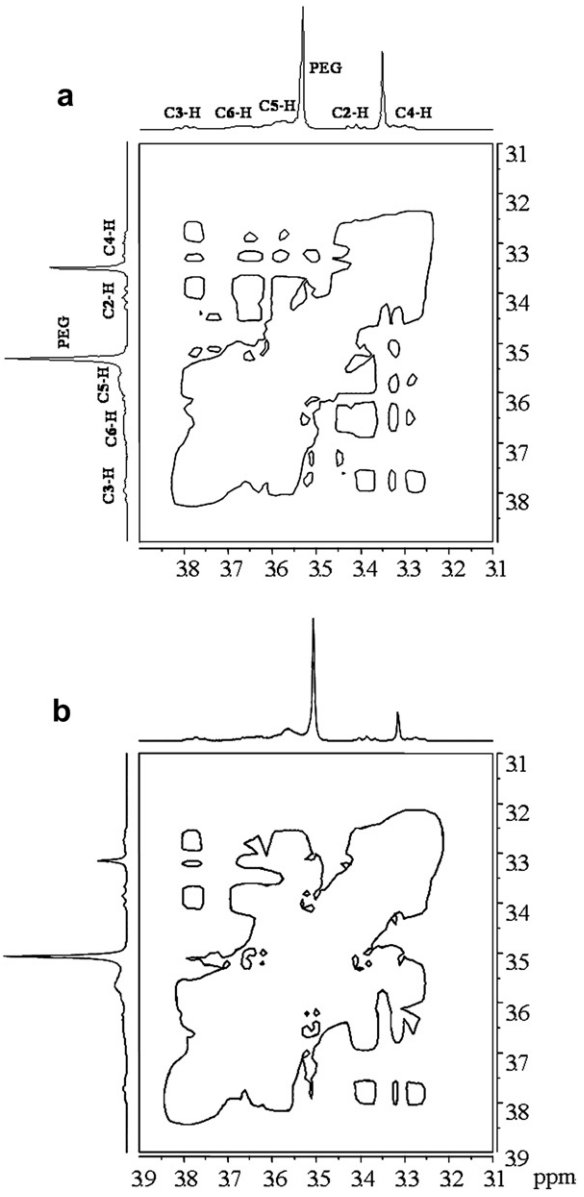


Fig. 4. 2D-NMR-NOESY spectra of (a) PEG_{3000}-CD-*co*-PMMA, (b) PEG_{6000}-CD-*co*-PMMA.

Fig. 5 shows g_{AB}(r) function between hydrogens of PEG (*a type* hydrogen) and cyclodextrines (C1 H, C2 H, C3 H, C4 H, C5 H and C6 H). It is observed a high probability for distances lower than 2.5 Å between hydrogen C3 H and C5 H of CDs and PEG hydrogen. The hydrogens C3 H and C5 H are located towards the inside of cyclodextrines cavity and consequently show the poly(rotaxan) formation. C1 H, C2 H, C4 H and C6 H hydrogen atoms show lower values mainly due to PEG chain fraction that are not forming poly(rotaxan) structures due possibly to low coverage in poly(rotaxan)s block copolymer.

The fraction of coupling (equation (2)), evaluated between the *a type* hydrogen (PEG), *b type* and *c type* (PMMA) (see Fig. 2) with C1 H, C2 H, C3 H, C4 H, C5 H and C6 H of cyclodextrines is shown in Table 2.

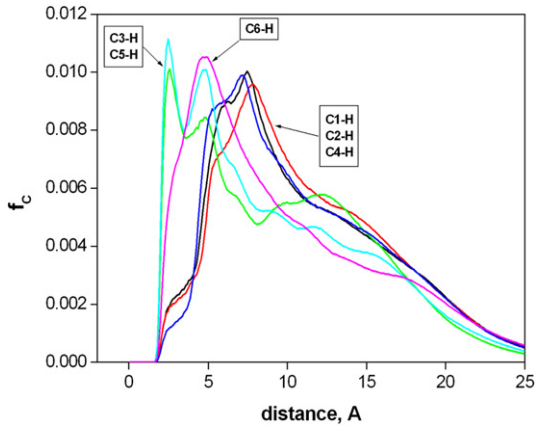


Fig. 5. Pair correlation function for the hydrogen coupling in PEG_{3000}-CD.

$$f_C \int_{r\ 0}^{r\ 2.5} g_{AB}(r)dr \quad (2)$$

Around 5% and 4% of *a type* hydrogens have a cyclodextrine hydrogen oriented towards the inside of the cavity at distance lower to 2.5 Å for PEG_{3000} CD *co* PMMA and PEG_{6000} CD *co* PMMA. Slightly smaller values of PEG_{6000} CD *co* PMMA were obtained and very small values have been obtained for hydrogens C1 H, C2 H and C4 H, located outside of cyclodextrine channel, due mainly to interactions of these hydrogen atoms with amorphous zone of poly(rotaxan)s and slightly higher values for PEG_{6000} CD *co* PMMA mainly due to the lower coverage as shown in the fifth column of Table 1.

The most important conclusion of the interactional analysis between *b* and *c type* atoms of PMMA and cyclodextrine hydrogens is the absence of interactions between these hydrogen atoms and C3 H and C5 H. This indicates that PMMA is not located inside the cyclodextrines channel, but is mainly forming the amorphous part of these copolymers.

4.3. X ray diffraction analysis

Wide angle X ray diffraction (WAXRD) is one of the most important methods to test the existence of "channel type" micro crystalline structure in the poly(rotaxan)s formed with α CDs [49]. The diffraction patterns of poly(rotaxan)s are shown in Fig. 6 together with the patterns corresponding to free α CD.

The peaks of free α CDs appear at 9.7°, 12.1°, 13.9° and 21.8°, respectively. The patterns of the poly(rotaxan)s are rather different from those obtained for free α CD and exhibit a strong peak at 2θ 20° characteristic of a tubular or "channel type" crystalline structure [49]. Furthermore, an amorphous halo in the

Table 2
Fraction of hydrogen coupling by molecular dynamics simulations. Hydrogen atoms (*a*) PEG, (*b*) and (*c*) PMMA and C–H cyclodextrine hydrogens (see Fig. 2).

f_C, %	PEG_{3000}-CD-*co*-PMMA			PEG_{6000}-CD-*co*-PMMA		
	a	*b*	*c*	*a*	*b*	*c*
C1-H	0.81	0.85	1.25	1.23	0.75	1.27
C2-H	0.80	0.70	1.49	1.38	0.10	1.50
C3-H	4.69	0.00	0.00	3.50	0.00	0.00
C4-H	0.49	0.14	0.79	0.94	0.21	0.67
C5-H	5.44	0.00	0.00	4.19	0.00	0.00
C6-H	2.18	0.58	1.05	1.79	0.50	0.74

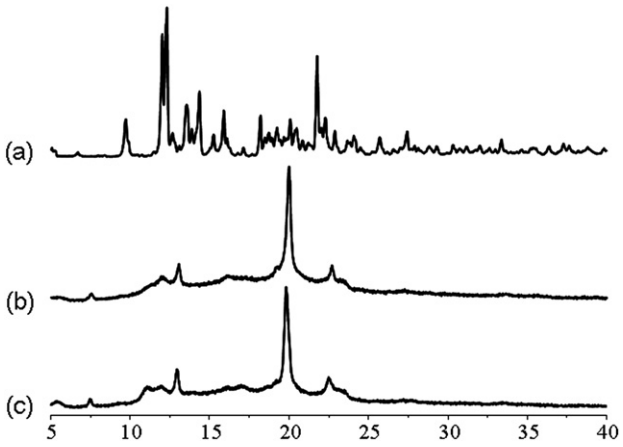


Fig. 6. XRD diffraction patterns of free α-CD (a), and poly(rotaxan) PEG_{3000}-CD-*co*-PMMA (b) and PEG_{6000}-CD-*co*-PMMA (c), respectively.

poly(rotaxan)s diffraction patterns attributed to PMMA blocks is observed and no signals corresponding to pure cyclodextrine crystals were observed, indicating that most α CDs are threaded onto the polymer chains. Similar results were obtained by Tong et al. with poly(rotaxan)s end capped with PHEMA [33].

Fig. 7 shows one representative conformation obtained by Molecular Dynamic simulation of PEG_{3000} CD *co* PMMA. In this figure the "channel type" crystalline structure formed by cyclo dextrines (in blue), in which the PEG chains are in *all trans* conformations [14], and the amorphous halo formed by the portion of PEG which is not inside the cyclodextrine channel (in yellow), as well as the PMMA block (in grey) can be observed. Possibly due to low coverage in poly(rotaxan)s, these complexes form small crystals in which the PEG blocks pertain simultaneously to several of them. These results agree with the characteristic tubular or "channel type" crystalline structure observed by XRD.

4.4. Thermal properties

Thermogravimetric analysis (TGA) of poly(rotaxan)s was performed in the range of 50 to 800 °C. The TGA thermograms are shown in Fig. 8. α CDs present a low weight loss around 100 °C primarily due to absorbed water and a fast weight loss at 325 °C

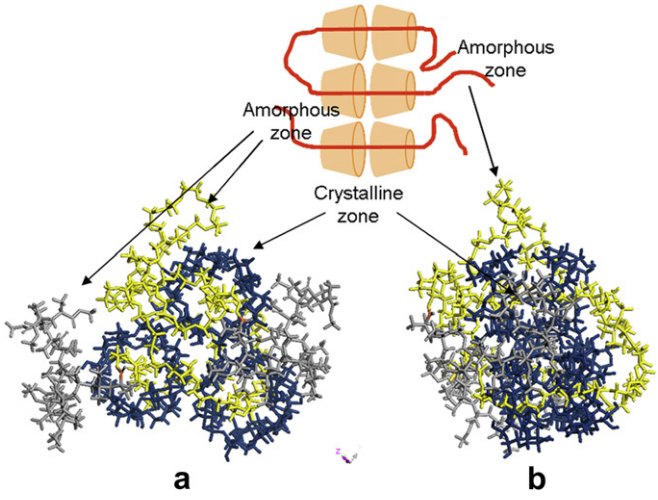


Fig. 7. One conformation of PEG_{3000}-CD-*co*-PMMA. Cyclodextrine (blue), PEG (yellow) and PMMA (grey). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

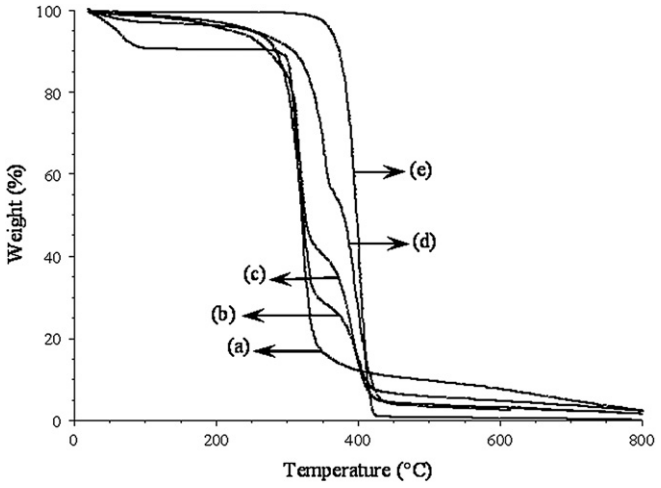


Fig. 8. TGA curves of (a) free α-CD, (b) pseudo-poly(rotaxan) PEG_{6000}-CD, triblock poly(rotaxan)s (c) PEG_{3000}-CD-*co*-PMMA and (d) PEG_{6000}-CD-*co*-PMMA and (e) PEG_{6000}.

while approximately 15 wt% residue remained at 500 °C. TGA profile of PEG_{6000} showed complete degradation of the complex in the range from 300 °C to 420 °C. On the other hand, TGA curves of the poly(rotaxan)s showed a two stage weight loss pattern attributed to the degradation of the α CDs and PEG PMMA [53] parts in temperature ranges from 250 °C to 350 °C and 350 °C to 420 °C respectively. It is worthy to note that the poly(rotaxan)s are stable in the range of temperatures used during the solvent elimination process. The first stage of decomposition correspond ing to α CD in the PEG_{6000} CD *co* PMMA triblock is risen by 20 °C compared with its free counterpart. Therefore, the α CD was significantly stabilized by the formation of the inclusion complex. This is also a direct proof of the existence of host guest supramo lecular interactions in the triblock poly(rotaxan)s.

Since α cyclodextrines and their inclusion compounds decom pose while melting, DSC scans of samples were performed below their melting temperature (i.e. below 200 °C). In Fig. 9, thermo grams (second run) obtained for (a) PEG_{3000} Br, (b) PEG *co* PMMA,

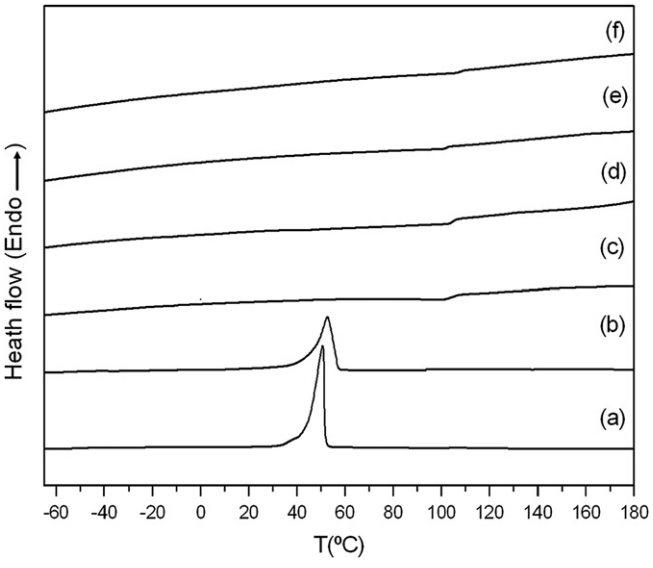


Fig. 9. DSC profiles of (a) PEG_{3000}-Br, (b) copolymer PEG-*co*-PMMA, (c) pure α-CD, (d) PEG_{3000}-CD, (e) poly(rotaxan)s PEG_{3000}-CD-*co*-PMMA and (f) PEG_{6000}-CD-*co*-PMMA.

(c) pure α CD, (d) PEG_{3000} CD pseudo poly(rotaxan) and poly (rotaxan)s: (e) PEG_{3000} CD *co* PMMA and(f) PEG_{6000} CD *co* PMMA are shown.

PEG_{3000} Br shows an endothermic peak at 51 °C, which corre sponds to its melting temperature. Melting temperature of the PEG block is also observed in PEG *co* PMMA triblock copolymer at 53 °C respectively, while T_g of the PMMA block is not observed. This behaviour is not uncommon in block copolymers, and has been previously reported for other PMMA PEG PMMA triblock copoly mers in which the PMMA blocks are shorter than the PEG block [50]. On the other hand, neither the pseudo poly(rotaxan) (*d*) nor the poly(rotaxan)s (*e* and *f*) show the characteristic PEG melting endothermic peak, indicating, in accordance with Tong et al [33], that there is not a sensible amount of free crystalline polymer and most of the polymer chains are inside the channels formed by neatly stacked α cyclodextrines. It is worthy to note that α CD does not show any relevant transition in the studied temperature range, although an endothermic feature is observed at 105 °C in all samples containing α CD; considering its highly hydrophilic character, it may be related to the presence of water in the cyclodextrine.

5. Conclusions

Triblock poly(rotaxan)s based in polyethyleneglycol end caped with poly(methyl methacrylate) have been successfully prepared by ATRP. A coverage degree of 15% and 18% was obtained for PEG_{3000} CD *co* PMMA and PEG_{6000} CD *co* PMMA respectively. This value is significantly lower than the coverage obtained for pseudo (polyrotaxane)s, indicating that unthreading of some cyclodextrines occurs during polymerization of PMMA chains.

Triblock copolymers show the typical X ray pattern of "tubular" or "channel type" structures and the amorphous halo corre sponding to PMMA blocks in the triblock poly(rotaxan)s is also observed. Calculations support the trend of poly(rotaxane)s to form an ordered structure, yielding the "channel type" structures observed by X rays.

2D NMR NOESY and Molecular Dynamics of these complexes show that the main interactions occur between C3 H and C5 H of cyclodextrines and PEG hydrogens; also that there are no interac tions between cyclodextrines and PMMA chains, indicating that the PMMA blocks are outside the channels and, therefore, liable to interact with other species in the medium. This is an important aspect for future applications of these compounds as nano reinforcements for polymer matrices, since it can be expected that the presence of the PMMA could enhance the complex solubility in certain polymer matrices, especially in epoxy systems. On the other hand, the absence of the PEG fusion endotherm in DSC thermo grams of both pseudo poly(rotaxane)s and poly(rotaxane)s is in agreement with the location of PEG block inside the tubular structure of cyclodextrines.

TGA shows that degradation of the triblock copolymers proceeds in two stages: first, decomposition of cyclodextrines between 250 °C and 300 °C, and afterwards PEG decomposition at higher temperatures (350 420 °C). Complexes are completely stable up to 200 °C, providing a quite wide range of temperatures for processing their mixtures with other polymers.

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